

[54] **SPACE-DYEING CELLULOSE FIBERS BY
IMPREGNATING WITH MIXTURE OF
DIAZONIUM**

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[75] Inventors: **Hans-Ulrich Von der Eltz;
Doris-Jutta Fink**, both of
Frankfurt/Main, Germany

Primary Examiner—George F. Lesmes
Assistant Examiner—Patricia C. Ives
Attorney, Agent, or Firm—Henry W. Koster et al.

[73] Assignee: **Farbwerke Hoechst
Aktiengesellschaft vormals Meister
Lucius & Bruning**, Frankfurt/Main,
Germany

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[58] **Field of Search**..... 8/14, 26, 46

[56] **References Cited**

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[57] **ABSTRACT**

Process for the space-dyeing of yarn or sliver made from cellulose fibers, wherein a wound package of the said textile material is first impregnated with an aqueous liquor containing an alkaline substance and at least one component capable of entering into azo coupling, and subsequently — at least at one selected portion of the bobbin — one or several weakly acid aqueous solutions each containing a mixture of at least two diazonium compounds of aromatic amines having different diffusibility are injected into the goods so treated for development of the azo dyestuffs.

1 Claim, No Drawings

SPACE-DYEING CELLULOSE FIBERS BY IMPREGNATING WITH MIXTURE OF DIAZONIUM

The present invention relates to a process for the space-dyeing of cellulose fibers.

From German Patent No. 1,244,104 it is known to dye yarn containing cellulose fibers with reactive dyestuffs irregularly in such a manner that no repetition of pattern occurs on the finished textile materials after the yarn thus dyed has been woven or knitted. According to this dyeing method known as "space-dyeing", an alkaline reactive dyestuff solution is injected into the wound-up fibrous material at different places and the wound package is then allowed to dwell until the dyestuff has reacted with the cellulose.

When, alternatively, direct dyestuffs are used for the injection solution according to this process, as disclosed in Austrian Patent No. 104,379, the yarn which has been space-dyed in this manner is not intended for use in certain textile articles since dyeings produced with these dyestuffs show poor fastness to wet processing. Dyeings produced with reactive dyestuffs have substantially better fastness properties in this respect, but the use of this dyestuff class known according to the prior art from German Patent No. 1,244,104 implies a relatively complicated process since prolonged dwelling times are required for the fixation of the dyestuffs on the fiber, thus reducing the production rate. Compared to the use of substantive dyestuffs, the production of dyeings with reactive dyestuffs has the additional disadvantage of generally involving substantially higher dyestuff costs.

Finally, according to the known methods for the space-dyeing of wound packages by injection of dyestuff solutions, the number of shades obtained in the bobbin depends on the number of injection locations chosen.

It has now been found that very fast multi-colored irregular dyeings can be obtained on cellulose yarn or sliver by injection of dyeing liquor into the wound-up fibrous material at least at one selected portion, at a favorable production rate and at reasonable dyestuff costs, especially for deep shades, the number of shades obtained being superior to that of injection locations chosen, by first impregnating the wound package of the textile material with an aqueous liquor containing alkaline substances and components capable of entering into azo coupling, and then injecting one or several weakly acid aqueous solutions containing mixtures of at least two diazonium compounds of aromatic amines having a different diffusing power, into the material thus treated for the development of the azo dyestuffs.

The coupling and diazo components used for the above-mentioned process as well as the coupling process itself are well known from the ice color technique. The development of azo dyestuffs on the fiber by the coupling of mixtures of several diazonium compounds with a single coupling component has also been in use for a long time. It was, therefore, especially surprising when it appeared in the course of the process of the invention that some of the diazo components have such a different diffusing power on cellulose material that it is possible to obtain, around the injection location, a core consisting of a mixed color and a peripheral zone differing therefrom in its shade, upon injection of a

mixture of diazo components of such diffusibility into a bobbin pre-treated with a coupling component. Similar effects have not yet been obtained upon dyeing from a long liquor in the dyeing apparatus as would correspond, on principle, to this injection method.

According to the process of the invention, pre-treatment of the wound-up yarns with the impregnation baths containing the alkaline substances and the coupling components is advantageously carried out in a dyeing apparatus, for example a device for dyeing cross-wound bobbins. This process step ensures simultaneous impregnation of a large number of bobbins and thus does practically not reduce the production rate, especially since the second lot can be already impregnated while the bobbins of the first lot are injected with the solution of the diazo components. Moreover, the wound packages pre-treated with alkali and coupling component can be stored and taken to use at any time and in any amount since the impregnated bobbins, after drying, are stable upon storage for an almost unlimited period of time if care is taken that any access of moisture is prevented.

For the impregnation of the wound-up yarn, coupling components are used, preferably those of substantive nature toward the fibrous material.

These are compounds which couple in vicinal position to a hydroxy group and do not have any solubilizing group, especially arylamides of aromatic or heterocyclic o-hydroxycarboxylic acids or of acylacetic acids, as well as other aromatic or heterocyclic hydroxy compounds and compounds containing an enolizable or enolized ketomethylene group in a heterocyclic ring. Such substances are, for example, the arylamides of 2,3-hydroxy-naphthoic acid, 2-hydroxyanthracene-3-carboxylic acid, 4-hydroxy-diphenyl-3-carboxylic acid, 2-hydroxy-carbazole-3-carboxylic acid, 3-hydroxy-diphenylene-oxide-2-carboxylic acid, 3-hydroxy-diphenylene-sulfide-2-carboxylic acid, aceto-acetic acid or of benzoylacetic acid. Furthermore, hydroxy-benzenes, polyhydroxy-benzenes, hydroxy-naphthalenes and pyrazolones have proved suitable among others, which may be substituted by non-ionic radicals.

As alkaline agents, any inorganic alkaline substance may be used in the impregnation baths; preferably sodium hydroxide solution. These baths may also contain commercial-type non-ionic or anionic wetting agents for a better penetration of the yarn; for example wetting agents on the basis of the reaction products of alkylene oxides with alkyl phenols, of mixtures consisting of high-molecular oxyalkylation products of alkanols or alkyl-phenols and alkyl-sulfuric acid esters of alkane- or alkyl-aryl-sulfonic acids, or of naphthalene-sulfonic acid derivatives.

The fibrous material is treated with the impregnation bath for 10 to 40 minutes, preferably for 30 minutes, at a temperature of from 20° to 50°C, preferably at room temperature.

After impregnation, the bobbins are centrifuged or sucked and can immediately be conducted to injection while still moist. Intermediate drying of the pre-treated goods is not necessary but it results in a higher liquor absorption during the subsequent injection since the fibrous material has a better absorptive power when dry.

As diazonium compounds for the development of the azo dyestuffs, any primary aromatic amine may be

used, which yields water-insoluble mono-, dis- or polyazo dyestuffs with the above-specified coupling components, thus the tetrazonium compounds of aromatic diamines and the fast color salts obtainable by stabilization from the corresponding amines, too. The said suitable amines, among them amino-azo dyestuffs, have no ionic substituents.

To those skilled in the art it is a very easy and quick task to determine the mixtures of diazo components suitable for the process of the invention. There is a great number of sample cards available from the dyestuff manufacturers for the choice of products of interesting shades. For testing the diazo components as to their diffusing power, aqueous solutions are prepared from the substances chosen, a mixture is composed from at least two of these solutions and a small amount of each solution is applied in a drop to a filter paper that has been preliminarily impregnated with the alkaline solution of a coupling component and dried. In the case of mixtures having constituents of different diffusing power, this test demonstrates that a peripheral zone having a shade different from that of the center of the drop applied is obtained on the substrate. By mixing more than two diazo components having a different diffusing power, the variety of shades obtained can substantially be increased. Accordingly, in the case of combinations of three components, it is possible exactly to recognize by the shade of the inner spot and by the peripheral zone or zones having a different color as well as by their breadth, whether — or to what extent — there is a different diffusing power of the individual constituents of the mixture. Starting from the center, the shade of these flow effects are gradually turning into the pure color of the dyestuff which is obtained from the diazo component having the most rapid and far-reaching diffusing power.

According to the process of the invention, the acid solution of the diazonium compounds is injected under pressure into the package that has been pre-treated with the coupling component, at least at one selected portion of the wound material. The coloring liquid thus spreads out along the limited injection zone, so that along the length of the yarn of the wound package, dyed and undyed areas of varying lengths are produced at quite irregular intervals. The amount of the diazonium compounds injected may, of course, be varied. It depends on the desired ratio of dyed and undyed yarn. The injection of the dyeing liquor at several locations may be carried out separately or simultaneously. To obtain a definite non-repeating pattern the injection positions must, of course, be selected in a suitable manner. In order to produce a multi-color spotted yarn according to the invention, diazonium solutions that yield patterns of different shades upon development with the coupling component may also be injected into the package, either separately or simultaneously.

The injection mechanism contains as the most essential element a hollow injection needle which has a perforated shaft (for more details see Astrodyed (registered trademark) Technical Manual, Astro Dye Works, Inc., Calhoun, Ga. 30701/USA, page 12, FIG. 14). The length of the needle approximately corresponds to the thickness of the wound package to be treated. The position of the injection needle support can be rearranged so that the point of the injection needle can penetrate the package from the outside yarn layer to a desired position inside the thickness of the winding, whereupon

the inflow of the dyeing liquor sets in. The flow of the liquor may be stopped again by a reversed motion of the needle support.

According to the novel process, generally weakly acid aqueous solutions of the diazo components are injected into the wound-up fibrous material. The pH value of these solutions is adjusted to 4.5 – 6.9 by means of known buffer mixtures or weak acids, especially acetic acid. In some cases, it is suitable to add commercial-type non-ionic dispersants, for example on the basis of the reaction products of alkylene oxides with cresol-camphor resins, or of mixtures consisting of oxyalkylated fatty alcohols and high-molecular-weight polyglycol ethers, to the injection solutions.

In most cases, injection liquors of about room temperatures are used.

In this respect, it surprisingly appeared that the degree of diffusion of the individual components can be varied by a special selection of the acid or alkali-binder used in the diazonium salt solutions to be injected.

Interesting fashionable effects can also be obtained by injecting, at one location of the bobbin, only a single diazo component which yields a deep blue shade, for example with the coupling component preliminarily applied, whereas solutions consisting of mixtures of diazo components having a different diffusibility are used for the other injection locations.

After injection of the diazo components, the bobbins are allowed to dwell for a short time, optionally for up to 5 minutes, and then after-treated as usual and dried. The dyeings produced according to the invention show the good fastness properties typical of the ice colors.

In the textile articles dyed according to the process of the invention the cellulose fibers may be present in natural or regenerated form. What has been said for the dyeing of yarn is also true for the dyeing of sliver.

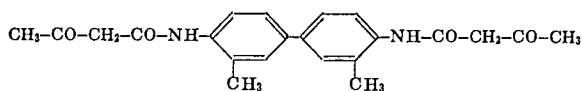
The following Example serves to illustrate the invention.

EXAMPLE

Six hundred and fifty Grams of wound-up cotton yarn were treated at 20°C for 30 minutes in a dyeing apparatus, at a goods-to-liquor ratio of 1 : 25, with the impregnation bath hereinafter disclosed. The wound package was then sucked and dried. At different locations of the bobbin, the below-indicated injection solutions (1) and (2) were injected into the ball of yarn thus impregnated, the liquor absorption of the fibrous material being 150 percent, calculated on the weight of the dry goods. The textile material dyed in this manner was then allowed to dwell for 5 minutes and then after-treated, in a dyeing apparatus, as usual and dried.

Impregnation bath

3.5 Grams of the compound of the formula



were dissolved in 3.5 cc. of denatured ethyl alcohol, 3.5 cc. of sodium hydroxide solution of 38°Be and 7 cc. of hot water. 5 Grams of a wetting agent on the basis of mixtures consisting of high-molecular-weight oxyalkylation products of alkanols or alkyl-phenols and alkyl-sulfuric acid esters of alkane- or alkylaryl-sulfonic acids were added to the solution thus obtained, and the li-

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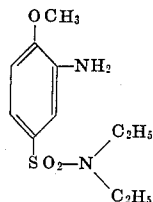
quor was adjusted to 1 liter by diluting with water of 30°C.

Injection solution 1

This solution contained a mixture of two about equal amounts by weight of the following solutions 1 (a) and 1 (b):

Solution 1 (a):

- 1 Liter of water contained
- 17 grams of the amine of the formula

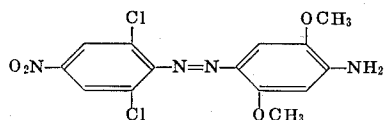


which had been diazotized by means of sodium nitrite and hydrochloric acid, the diazonium salt solution obtained having been neutralized by adding sodium acetate,

- 3.5 cc. of acetic acid (of 50 percent strength) and
- 1 gram of a dispersing agent on the basis of mixtures consisting of oxyalkylated fatty alcohols and high-molecular-weight polyglycol ethers.

Solution 1 (b):

- 1 Liter of water contained
- 72 g of the amino azo dyestuff of the formula



which had been diazotized by means of sodium nitrite and hydrochloric acid,

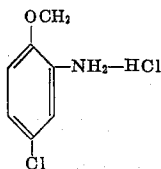
- 20 cc. of acetic acid (of 50 percent strength) and
- 1 g of a dispersing agent as indicated sub solution 1 (a).

Injection solution 2

This solution contained a mixture of two about equal amounts by weight of the following solutions 2 (a) and 2 (b):

Solution 2 (a):

- 1 Liter of water contained
- 13 g of the amine of the formula



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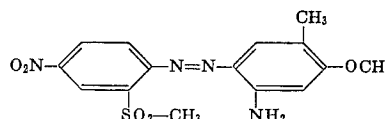
which had been diazotized by means of sodium nitrite and hydrochloric acid and the diazonium salt solution obtained had been neutralized by means of sodium acetate,

- 1 g of a dispersing agent as indicated sub solution 1 (a),
- 4 cc. of acetic acid (of 50 percent strength) as well as a preliminary addition of
- 7 to 10 g of sodium acetate.

10 Solution 2 (b):

- 1 Liter of water contained
- 100 g of the aminoazo dyestuff of the formula

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- 20 which had been diazotized by means of sodium nitrite and hydrochloric acid, and the diazonium compound obtained had been dissolved by pouring over a mixture of 500 cc. of luke-warm water, 5 cc. of a reaction product of alkylene oxides with cresol-camphor resins and
- 25 60 cc. of acetic acid (of 50 percent strength). By adding cold water, this solution was adjusted to 1,000 cc. and 10 g of sodium acetate and 10 to 40 cc. of acetic acid (of 50 percent strength) were added.

A bobbin was obtained, the yarn of which showed, in the core of the injection location, an intense brown red shade with mixed solution 1 and, at the corresponding peripheral zone, a yellow shade in a reduced breadth. The mixed solution 2 yielded, in the center of the injection location, a medium brown shade and, in the quite large peripheral zone, a bright brilliant golden yellow shade.

Corresponding results to those of the preceding Example can be obtained using cellulose sliver for the dyeings instead of yarn.

What we claim is:

- 1. In a process for the space-dyeing of yarn or sliver made from cellulose fibers by injection of dyeing liquid into the fibrous material at least at one selected portion of the wound package, the improvement which comprises: first impregnating a bobbin of the said textile material with an aqueous liquor containing sodium hydroxide and at least one coupler component capable of entering into azo coupling; and subsequently injecting the so treated bobbin, for development of the azo dyestuffs, with at least one weakly acid solution having a pH value in the range of from 4.5 to 6.9, each of said solutions containing a mixture of at least two diazonium compounds of aromatic amines having different diffusibility.

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